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(54) COATING COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composition which has a low refractive index suitable for antireflecting film on a photoresist surface and can be completely removed by developer during developing of the photoresist by using a fluorine-based polymer containing a specific polymerization unit.

SOLUTION: A fluorine-based polymer to be used contains a polymerization unit represented by -CF₂CF(ORfCOOM)- or both the above polymerization unit and a polymerization unit represented by -CF₂CFX- (Rf is a linear or branched perfluoroalkylene which may contain an ether oxygen; -COOM includes -COOH, -COOY (Y is a non-substituted or substituted ammonium ion) and -COOH.Z (Z is an amine); and X includes fluorine and chlorine). Number average molecular weight of the fluorine-based polymer is preferably 1×10³-3×10⁴. A solvent to be used is water, an organic solvent or a mixture of water and an organic solvent.

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CLAIMS

[Claim(s)]

[Claim 1] The coating constituent characterized by containing a fluorine system polymer including the polymerization unit expressed with the polymerization unit expressed with a fluorine system polymer or the following type 1 including the polymerization unit expressed with the following type 1, and the following type 2.

[Formula 1] - CF₂ CF(ORfCOOM)- Formula 1-CF₂ CFX- formula 2[-- the perfluoro-alkylene group of the shape of a straight chain in which Rf may also contain an ether nature oxygen atom, and the letter of branching, and -COOM are -COOH, -COOY (ammonium ion by which Y may be permuted), or -COOH-Z (Z is an amine) among a formula, and X is a fluorine atom or a chlorine atom.]

[Claim 2] the number average molecular weight of a fluorine system polymer -- 1x10³ to 3x10⁴ it is -- coating constituent according to claim 1.

[Claim 3] The pattern formation approach characterized by using the photoresist layer which has the antireflection film formed in the photoresist layer front face from the coating constituent according to claim 1 or 2 in forming a pattern by the photolithography using a photoresist.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a coating constituent useful as an antireflection coating constituent used in the case of the photolithography using the photoresist in semi-conductor manufacture etc.

[0002]

[Description of the Prior Art] In case the pattern of a photoresist is formed by the photolithography, multiplex interference of the light by light reflecting in the interface and photoresist layer front face of a photoresist layer and a base material at the time of exposure reduces pattern dimensional accuracy. The approach of forming an antireflection film in a photoresist layer front face conventionally is examined in order to prevent this. It is supposed that what generally has the following engine performance is desirable as an antireflection film.

[0003] (1) Since the acid-resisting effectiveness serves as max by the well-known acid-resisting theory when the refractive index of the antireflection film is equal to the square root of the refractive index of a photoresist, it is desirable that it is close to the value as much as possible. Specifically, it is anxious for the antireflection film with a refractive-index value smaller than 1.4. To the refractive indexes 1.6-1.8 of a general photoresist, as for the refractive index of an antireflection film, 1.27-1.34 are ideal, and acid resistibility ability falls, so that the gap from this value becomes large.

[0004] (2) It is desirable to perform clearance of the antireflection film with the developer of a photoresist. Although development of the photoresist after exposure is performed by alkali water solutions, such as a tetramethylammonium hydroxide water solution, it is more desirable than the viewpoint of process compaction and the improvement in the yield to also remove an antireflection film simultaneously in this case.

[0005] various antireflection films are indicated until now -- **** (JP,62-62521,A, JP,5-188598,A, JP,6-148896,A, JP,8-305032,A, JP,9-50129,A, JP,9-90615,A) -- the refractive index of these antireflection films was 1.4 to about 1.5 practically, and since the deviation from an ideal refractive-index value was large, it was not able to discover sufficient acid resistibility ability.

[0006] the antireflection film which has an ideal refractive-index value of 1.3-1.34 is also indicated -- **** (JP,62-62520,A, JP,5-74700,A) -- in order not to dissolve in an alkali water solution, before photoresist development, these needed to remove the film with the special solvent and had caused the increment in a routing counter, and lowering of the yield.

[0007] the antireflection film which a refractive index is smaller than 1.4 and dissolves also in an alkali water solution to some extent is also indicated -- **** (JP,6-180168,A) -- since the amount of saturation dissolutions and dissolution rate to an alkali water solution are not enough, the dissolution residue of the minute amount generated at the time of photoresist development causes yield lowering, and has not resulted in utilization.

[0008]

[Problem(s) to be Solved by the Invention] This invention aims at offering the coating constituent useful

as an antireflection coating constituent for photoresists etc. with which sufficient solubility over an alkali water solution and a refractive-index value smaller than 1.4 are compatible.

[0009]

[Means for Solving the Problem] This invention is a coating constituent characterized by containing a fluorine system polymer including the polymerization unit expressed with the polymerization unit expressed with a fluorine system polymer or the following type 1 including the polymerization unit expressed with the following type 1, and the following type 2. However, the perfluoro-alkylene group of the shape of a straight chain in which Rf may also contain an ether nature oxygen atom, and the letter of branching, and -COOM are -COOH, -COOY (ammonium ion by which Y may be permuted), or -COOH-Z (Z is an amine) among a formula, and X is a fluorine atom or a chlorine atom.

[0010]

[Formula 2] - CF₂ CF(ORfCOOM)- Formula 1-CF₂ CFX- Formula 2 [0011] The fluorine system polymer in this invention is a fluorine system polymer including the polymerization unit expressed with the polymerization unit expressed with a fluorine system polymer or formula 1 including the polymerization unit expressed with a formula 1, and a formula 2.

[0012] Rf in a formula 1 is the perfluoro-alkylene group of the shape of a straight chain which may also contain an ether nature oxygen atom, and the letter of branching. As for the carbon number of a perfluoro-alkylene group, 1-10 are desirable from the ease of acquisition etc., and 2-7 are more desirable. Although an ether nature oxygen atom usually exists between the carbon of a perfluoro-alkylene group, you may exist between the carbon of -COOM in a formula 1, and the carbon of a perfluoro-alkylene group.

[0013] - COOM is -COOH, -COOY (ammonium ion by which Y may be permuted), or -COOH-Z (Z is an amine). X in a formula 2 is a fluorine atom or a chlorine atom.

[0014] As ammonium ion by which said Y may be permuted, what permuted one or more [of the hydrogen atom of NH₄⁺ and NH₄⁺] by organic radicals, such as an alkyl group, an acid radical, and a hydroxyl group, is mentioned.

[0015] As an amine of said Z, if the object of this invention is not barred, one or more sorts of the compound of well-known common knowledge can be used. For example, alkanolamines, such as alkylamine, such as dialkyl amines, such as monoalkyl amines, such as ethylamine and propylamine, and diethylamine, and triethylamine, ethanolamine, and diethanolamine, are mentioned.

[0016] Although a fluorine system polymer has the polymer which consists only of a polymerization unit expressed with a formula 1, or desirable polymer [which consists only of a polymerization unit expressed with the polymerization unit expressed with a formula 1, and a formula 2] **, the polymer which includes polymerization units other than the polymerization unit expressed with the polymerization unit and formula 2 which are expressed with a formula 1 less than [10 mol %] is sufficient as it.

[0017] As polymerization units other than the polymerization unit expressed with the polymerization unit and formula 2 which are expressed with a formula 1, the polymerization unit based on polymerization nature perfluoro-compounds, such as perfluoro-vinyl ether and with a carbon numbers of three or more perfluoro-olefins, is mentioned.

[0018] In a fluorine system polymer including the polymerization unit expressed with the polymerization unit expressed with a formula 1, and a formula 2, as for the rate of the polymerization unit expressed with a formula 1 to the sum total of the polymerization unit expressed with the polymerization unit and formula 2 which are expressed with a formula 1, less than [100 mol %] is desirable at more than 40 mol %, and less than [100 mol %] is more desirable at more than 50 mol %. the rate of the polymerization unit expressed with a formula 2 to the sum total of the polymerization unit expressed with the polymerization unit and formula 2 which are expressed with a formula 1 -- zero-mol % -- super- -- less than [60 mol %] -- desirable -- zero-mol % -- super- -- less than [50 mol %] is more desirable. The solubility over the alkali water solution of a fluorine system polymer improves by making the rate of the polymerization unit expressed with a formula 1 more than 40 mol %.

[0019] the number average molecular weight of a fluorine system polymer -- 1x10³ to 3x10⁴ it is --

things -- desirable -- 2×10^3 to 2×10^4 it is -- things are more desirable. Number average molecular weight is 1×10^3 . In the following, film formation nature gets worse remarkably, and the uniform coating film cannot be obtained, and it is 3×10^4 . ** may not be enough as the solubility over an alkali water solution.

[0020] The coating constituent of this invention usually dissolves the above-mentioned fluorine system polymer into a solvent. As a solvent, the mixed solvent of water, an organic solvent, or a water and an organic solvent can be used. Especially the coating constituent of this invention is useful as an antireflection coating constituent applied to a photoresist layer etc. As a solvent of an antireflection coating constituent, in case an antireflection coating constituent is applied to a photoresist layer, it is desirable to choose from what does not give a damage to the photoresist film.

[0021] As a desirable example of a solvent, the mixed solvent of water independence or water, and alcohols, such as a methanol, ethanol, isopropanol, 2, 2, 3 and 3, and 3-pentafluoro propanol, is mentioned. If there are many rates of the alcohols in a mixed solvent, since a damage may be given to a photoresist layer, for example, 40 or less % of the weight is desirable, and 20 or less % of the weight is still more desirable.

[0022] Although what is necessary is just to set up the concentration of the fluorine system polymer in a coating constituent so that it will not be limited especially if it is within the limits which a fluorine system polymer dissolves, but desired coating thickness can be obtained, it is usually 1 - 10% of the weight of the range.

[0023] Surfactants, such as an amine salt of a fluorine system organic acid, can be added for the object of improving the wettability at the time of spreading, and the homogeneity of a paint film to the constituent of this invention. Since too many additions cause milkiness of a paint film or have a possibility of it being spread in the photoresist film of an antireflection-film lower layer, and causing poor exposure when there are, its 10 or less % of the weight is desirable to a fluorine system polymer, and its 5 or less % of the weight is still more desirable.

[0024] In forming a pattern by the photolithography using a photoresist, the photoresist layer which has the antireflection film formed in the photoresist layer front face from the coating constituent of this invention can be used.

[0025] As an approach of forming an antireflection film in a photoresist layer front face with the constituent of this invention, a spin coat method is suitably adopted from the viewpoint of the homogeneity of a paint film, and simple nature. Moreover, it is usually common behind a coat to dry in a hot plate or oven in order to remove a solvent. In the case of a hot plate, as desiccation conditions, the conditions for 30 - 200 seconds are illustrated at the temperature of 80-100 degrees C, for example.

[0026] Since acid resistibility ability becomes large, as for the thickness of an antireflection film, it is [that what is necessary is just to set up according to the well-known acid-resisting theory] desirable to make thickness into odd times of λ (exposure wavelength) ($4 \times$ (refractive index of an antireflection film))."

[0027] When using the coating constituent of this invention as an antireflection coating constituent of a photoresist layer, there is especially no limit in an applicable photoresist, and effectiveness is demonstrated to the photoresist for excimer lasers, such as an object for g lines, an object for i lines, or ArF, KrF. Especially the paint film formed with the constituent of this invention although a resist front face may deteriorate if the neglect time amount in the inside of the atmospheric air after exposure becomes long when the photoresist of an antireflection-film lower layer is the so-called chemistry magnification mold resist using the catalysis of the proton generated by exposure acts also as a protective coat which prevents the deterioration.

[0028]

[Example] Although a synthetic example (Examples 1-2) and an example (Examples 3-6) are given and this invention is explained still more concretely hereafter, this invention is not limited to these.

[0029] [Example 1] $\text{CF}_2 = \text{CFOCF}_2 \text{CF}_2 \text{COOCH}_3$ 306g was taught to 500 cc autoclave with an agitator, nitrogen permuted the inside of a system, and it was made G the internal pressure of 1 kg/cm^2 . 86g of 5%HCFC-225 (1, 3-dichloro - 1, 1, 2, 2, 3-pen TAFURORO propane) solutions of perfluoro-

butanoyl peroxide -- adding -- an internal temperature -- 40 degrees C -- temperature up -- the polymerization reaction was carried out. Internal pressure rose to G by 1.8kg/cm² 5.5 hours after, and after that, lifting of internal pressure was no longer seen and was considered as polymerization termination.

[0030] It is CF₂=CFOCF₂ CF₂ COOCH₃ by heating and reduced pressure to distilling off and a pan about HCFC-225 at reduced pressure after polymerization termination. It distilled off. obtained CF₂=CFOCF₂CF₂ COOCH₃ the place which calculated the number average molecular weight of a homopolymer by the GPC method -- about 4.5x10³ it was .

[0031] By hydrolyzing this homopolymer, the fluorine system polymer (henceforth Polymer A) which consists of polymerization unit-CF₂ CF(OCF₂CF₂ COOH)- was obtained. Furthermore, the aqueous ammonia solution performed ammonium salt-ization of Polymer A 29%, superfluous ammonia and water were distilled off, and the fluorine system polymer (henceforth Polymer B) which consists of polymerization unit-CF₂ CF(OCF₂ CF₂ COONH₄)- was obtained.

[0032] [Example 2] CF₂=CFOCF₂ CF₂ COOCH₃ 3g of 5%HCFC-225 solutions of 220g and perfluoro-butanoyl peroxide was taught to 200 cc autoclave with an agitator, and nitrogen permuted the inside of a system. After cooling and deaerating this system with liquid nitrogen, TFE

(tetrafluoroethylene)9g was introduced and it was made G the internal pressure of 2.5kg/cm². further -- an internal temperature -- 40 degrees C -- temperature up -- the polymerization reaction was carried out.

[0033] Internal pressure descended to G by 1.2kg/cm² 3.0 hours after, and after that, descent of internal pressure was no longer seen and was taken as polymerization termination. TFE is purged after polymerization termination and it is CF₂=CFOCF₂ CF₂ COOCH₃ by heating and reduced pressure to distilling off and a pan about HCFC-225 at reduced pressure. It distilled off.

[0034] Obtained CF₂=CFOCF₂ CF₂ COOCH₃ The copolymer of TFE was what contains CF₂=CFOCF₂ CF₂ COOCH₃ / TFE by 1/1 of mole ratios by the F-NMR method. moreover, the place which calculated the number average molecular weight of this copolymer by the GPC method -- about 8.7x10³ it was .

[0035] By hydrolyzing this copolymer, the fluorine system polymer (henceforth Polymer C) which consists of polymerization unit-(CF₂ CF₂)- and polymerization unit-CF₂ CF(OCF₂ CF₂ COOH)- was obtained. Furthermore, the aqueous ammonia solution performed ammonium salt-ization of Polymer C 29%, superfluous ammonia and water were distilled off, and the fluorine system polymer (henceforth Polymer D) with which polymerization unit-(CF₂ CF₂)- and polymerization unit-CF₂ CF(OCF₂ CF₂ COONH₄)- consist of mole ratios 1/1 was obtained.

[0036] [Example 3] Polymer A was dissolved in water / methanol mixed solvent (20 % of the weight of methanol contents), the constituent for antireflection coating of 5 % of the weight of polymer concentration was prepared, and next assessment 1 and assessment 2 were performed. Consequently, the refractive index was 1.36 and thickness was 67nm. Moreover, on the pattern of a photoresist, residue, a foreign matter, etc. were not observed but it checked that the antireflection film was thoroughly removable at the time of resist development.

[0037] (Assessment 1: The refractive index of a paint film, and measurement of thickness) The constituent for antireflection coating was applied on the silicon wafer with the spin coat method, and the refractive index and thickness of a paint film were measured by the ellipsometer.

[0038] (Assessment 2: Assessment of the antireflection-film clearance property at the time of photoresist development) On the silicon wafer which carried out surface preparation, the resist layer of 1 micrometer of thickness was formed by drying 90 degree C of photoresist THMR-iP1700 (TOKYO OHKA KOGYO CO., LTD. make) for 90 seconds on spreading and a hot plate with a spin coat method by leaving it for 5 minutes in a hexa methyl silazane ambient atmosphere.

[0039] Subsequently, when the spin coat of the constituent for antireflection coating was carried out and 90 degrees C dried for 60 seconds on a hot plate, the acid-resisting layer was formed. The spin coat conditions at this time were made into the same conditions as assessment 1. Next, it exposed by i line (365nm) through the test pattern, and after [the postexposure] BEKU (PED) was performed. Subsequently, after performing paddle development for 65 seconds using a developer (2.38-% of the

weight tetramethylammonium hydroxide water solution), the rinse was carried out with ultrapure water and the pattern of a photoresist was obtained.

[0040] Metaloscope observation was performed about this sample and it evaluated whether the antireflection film had fully removed at the time of development.

[0041] [Example 4] Assessment 1 and assessment 2 were performed like Example 3 except having changed Polymer A into Polymer B. A result is shown below.

(Assessment 1) A refractive index 1.37, 66nm of thickness.

(Assessment 2) On the pattern of a photoresist, residue, a foreign matter, etc. were not observed but it checked that the antireflection film was thoroughly removable at the time of resist development.

[0042] [Example 5] Assessment 1 and assessment 2 were performed like Example 3 except having changed Polymer A into Polymer C. A result is shown below.

(Assessment 1) A refractive index 1.35, 68nm of thickness.

(Assessment 2) On the pattern of a photoresist, residue, a foreign matter, etc. were not observed but it checked that the antireflection film was thoroughly removable at the time of resist development.

[0043] [Example 6] Polymer A was changed into Polymer D and assessment 1 and assessment 2 were performed like Example 3 except having made the solvent water independent. A result is shown below.

(Assessment 1) A refractive index 1.37, 66nm of thickness.

(Assessment 2) On the pattern of a photoresist, residue, a foreign matter, etc. were not observed but it checked that the antireflection film was thoroughly removable at the time of resist development.

[0044]

[Effect of the Invention] This invention is useful as a coating constituent which can form the antireflection film which has a low refractive index suitable as antireflection film on the front face of a photoresist layer, and can be especially removed thoroughly with a developer at the time of photoresist development. By using this constituent, it contributes to high yield-ization of a pattern formation process.

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CORRECTION OR AMENDMENT

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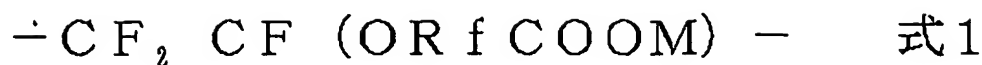
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[Procedure amendment]
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[Procedure amendment 1]
 [Document to be Amended] Description
 [Item(s) to be Amended] Claim
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 [Claim(s)]

[Claim 1] The coating constituent characterized by containing a fluorine system polymer including the polymerization unit expressed with the polymerization unit expressed with a fluorine system polymer or the following type 1 including the polymerization unit expressed with the following type 1, and the following type 2.

[Formula 1]



[-- the perfluoro-alkylene group of the shape of a straight chain in which Rf may also contain an ether nature oxygen atom, and the letter of branching, and -COOM are -COOH, -COOY (ammonium ion by which Y may be permuted), or -COOH-Z (Z is an amine) among a formula, and X is a fluorine atom or a chlorine atom.]

[Claim 2] The coating constituent according to claim 1 whose number average molecular weight of a fluorine system polymer is 1×10^3 to 3×10^4 .

[Claim 3] The coating constituent according to claim 1 or 2 said whose coating constituent is a ***** coating constituent for photoresists.

[Claim 4] The pattern formation approach characterized by using the photoresist layer which has the antireflection film formed in the photoresist layer front face from the coating constituent according to claim 1, 2, or 3 in forming a pattern by the photolithography using a photoresist.

[Translation done.]